

APPENDIX

EXPERIMENTAL METHODS

CHEMICAL STANDARDS (for Methods Developed at MWDSC)

When commercial standards were not available, standards were synthesized for the project. The initial phase of the project required a survey of chemical companies to obtain as many of the target compounds as possible. The remaining compounds were then synthesized. This led to a step-wise approach to incorporating compounds as they became available for analysis. When synthesized materials were prepared in less than 10-mg allotments, additional standards were sometimes needed later in the project.

At Metropolitan Water District of Southern California (MWDSC), multiple methods were used to test for DBPs. It was necessary to make up two independent sets of stock solutions, in methyl *tertiary* butyl ether (MtBE) and methanol, depending on the solvent requirements of each technique. Each “pure” standard from the MtBE set was characterized individually to determine whether there were any impurities, to note what the impurities were and at what level (percentage). Many of the discovered impurities were, in fact, other DBPs. When all the standards were combined into spiking solutions, any additionally added DBPs (impurities) had to be accounted for through the use of correction factors, either to the final results or to the standards being used to generate calibration curves. When correction factors were applied, reported concentrations were more accurate because they reflected the true composition of the combined set of calibration standards.

Stock Solutions

Several commercially available certified standards and mixes were purchased (Table 1). These mixes were spiked directly or used to create additional compound class mixtures for calibration purposes and spikes of unknown samples.

Typically, at the beginning of each quarter, new stock solutions were prepared in MtBE and methanol. In September 2000, the first set was created that would last through the Fall 2000 quarter’s sampling. The next set of stock solutions covered all of the Winter 2001 quarter and the samples from early Spring 2001. Another set was created in May 2001 and was used through the end of the year, covering both Summer and Fall 2001 quarter’s samplings. The last set of stock solutions was made in January 2002, and was used with the final phase of sampling in the Winter 2002 quarter and an early Spring 2002 sampling.

The MtBE-diluted compounds were tested in full-scan mode to verify the electron impact (EI) mass spectrum of the pure compound and also to check for impurities or degradation products present (Figures 1-7). As part of an on-going check of the standards, the individual stock solutions would be periodically checked to note any changes in the calculated purity or the impurities present. Initially, the solutions were checked every 4-6 weeks. Subsequently, after approximately 3 month’s usage, new stock solutions would be created, and the previous set stored for future reference.

Table 1. Certified commercial standards used at MWDSC

Certified Mixes	Compound	Standards Used in Method ^a		
		LLE-GC/ECD	P&T-GC/MS	SPE-GC/MS
Bromochloromethane Supelco 4-8067 2000 µg/mL in methanol	Bromochloromethane		X	
Carbon Tetrachloride Supelco 40360-U 5000 µg/mL in methanol	Carbon tetrachloride		X	
Chloral Hydrate Supelco 4-7335-U 1000 µg/mL in acetonitrile	Chloral hydrate	X		
Dibromomethane Supelco 4-8339 2000 µg/mL in methanol	Dibromomethane		X	
EPA 524.2 Fortification Solution Supelco 47358-U 2000 µg/mL in methanol	4-Bromofluorobenzene 1,2-Dichlorobenzene-d4 Fluorobenzene		X X X	
EPA 551B Halogenated Volatiles Supelco 4-8046 2000 µg/mL in acetone or HCM-551B (Ultra Scientific) 5000 µg/mL in methanol	Bromochloroacetonitrile Chloropicrin Dibromoacetonitrile Dichloroacetonitrile 1,1-Dichloropropanone Trichloroacetonitrile 1,1,1-Trichloropropanone	X X X X X X X	 X X X X	X X X X X X X
EPA 624 Calibration Mix B Supelco 46967-U 2000 µg/mL in methanol	Bromomethane Chloroethane Chloromethane Trichlorofluoromethane Vinyl chloride		X X	
Methyl Tert-Butyl Ether Supelco 4-8483 2000 µg/mL in methanol	Methyl <i>tert</i> -butyl ether		X	
Trihalomethane Calibration Mix Supelco 4-8140-U, 2000 µg/mL in MeOH or THM-521 (Ultra Scientific) 5000 µg/mL in methanol	Bromodichloromethane Bromoform Chloroform Dibromochloromethane	X X X X	X X X X	X X X X
2-Butanone Supelco 4-8877 2000 µg/mL in MeOH/H ₂ O 90:10	Methyl ethyl ketone		X	

^aLLE-GC/ECD: Liquid/liquid extraction-gas chromatography/electron capture detection

P&T-GC/MS: Purge-and-trap - GC/mass spectrometry

SPE-GC/MS: Solid-phase extraction - GC/MS

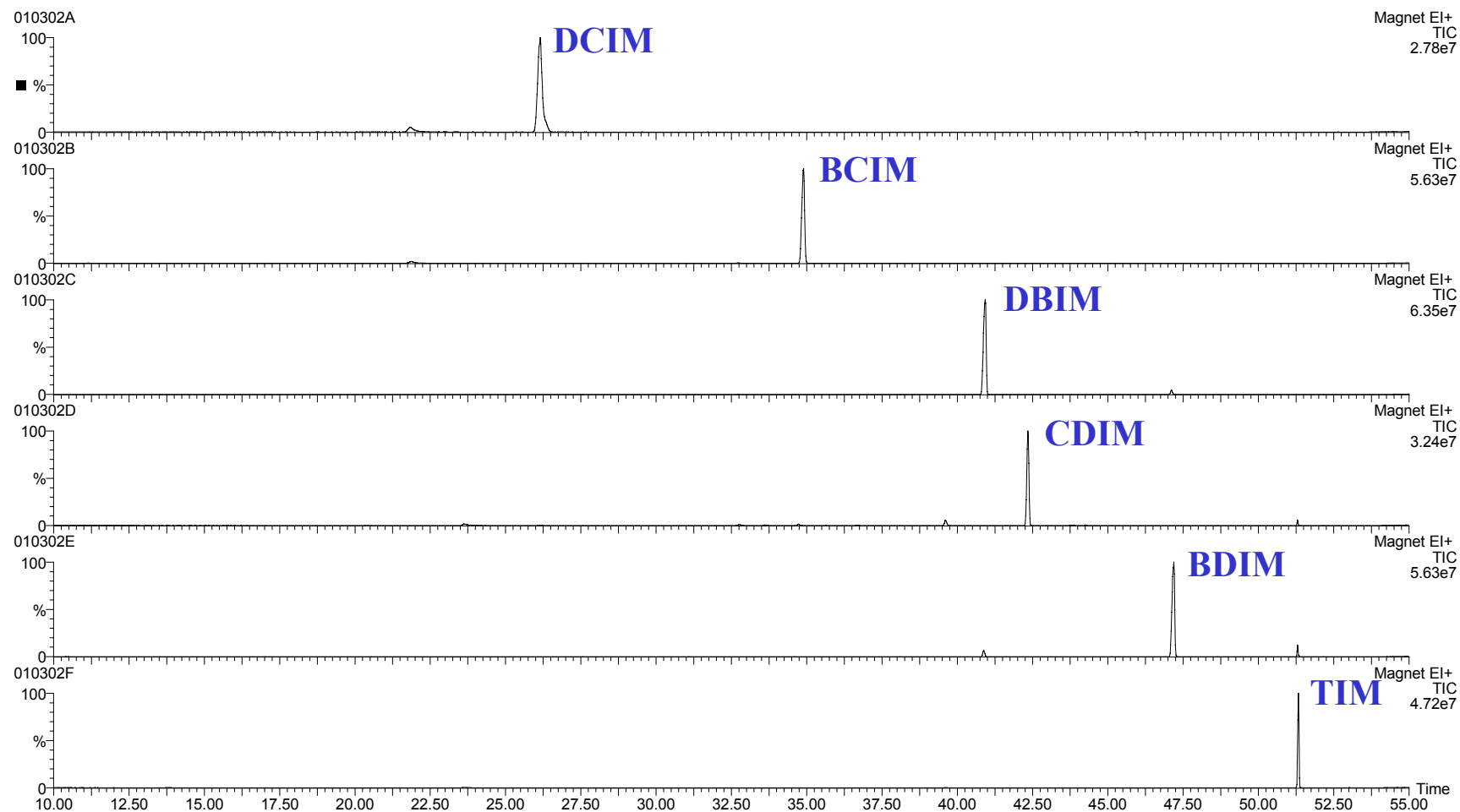


Figure 1. Full-scan total ion chromatograms of iodomethanes from January 2002 stock solution. DBP abbreviations provided in Table 2.

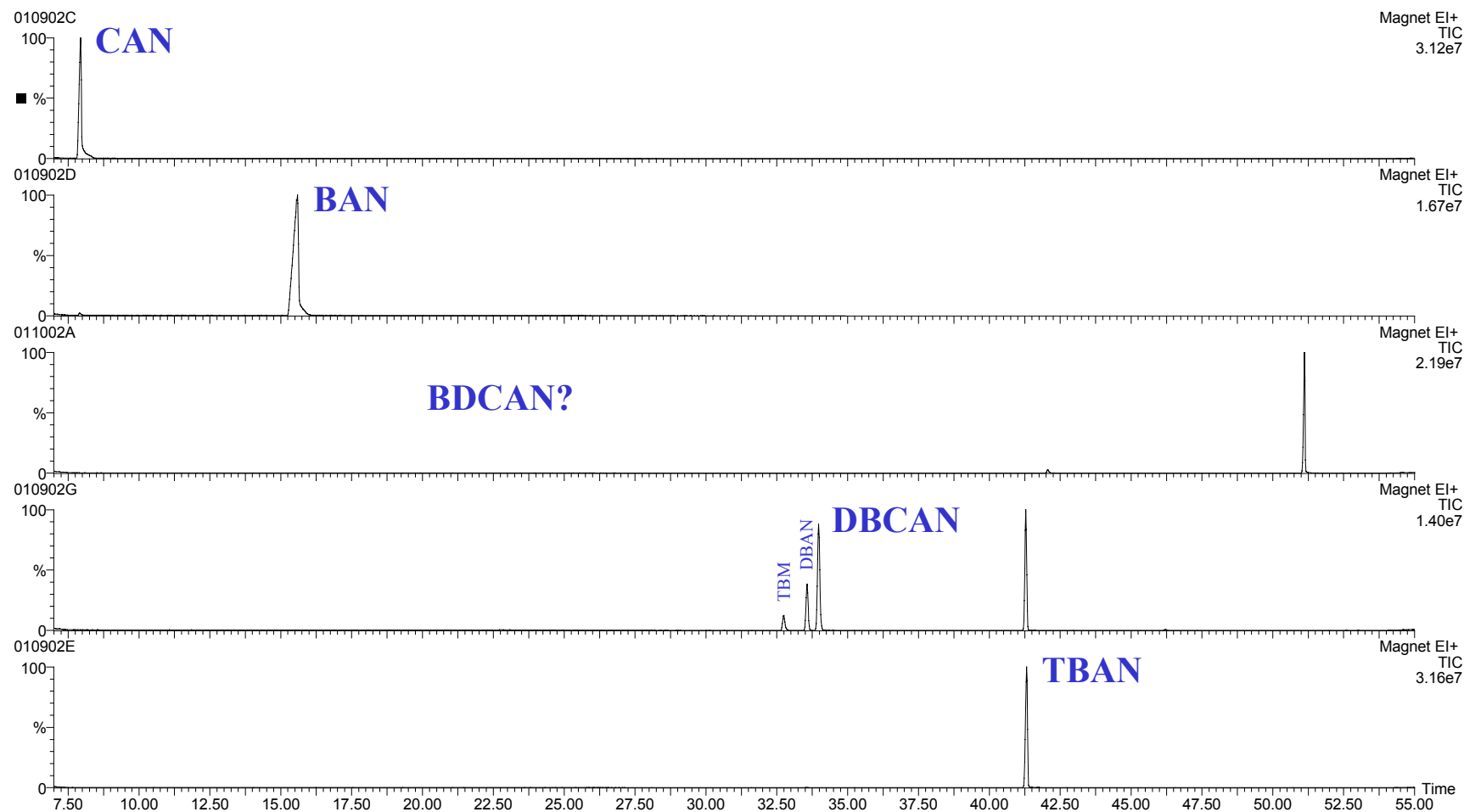


Figure 2. Full-scan total ion chromatograms for haloacetonitriles from January 2002 stock solution; a poor result for bromodichloroacetonitrile required the use of the May 2001 stock solution. DBP abbreviations provided in Table 2.

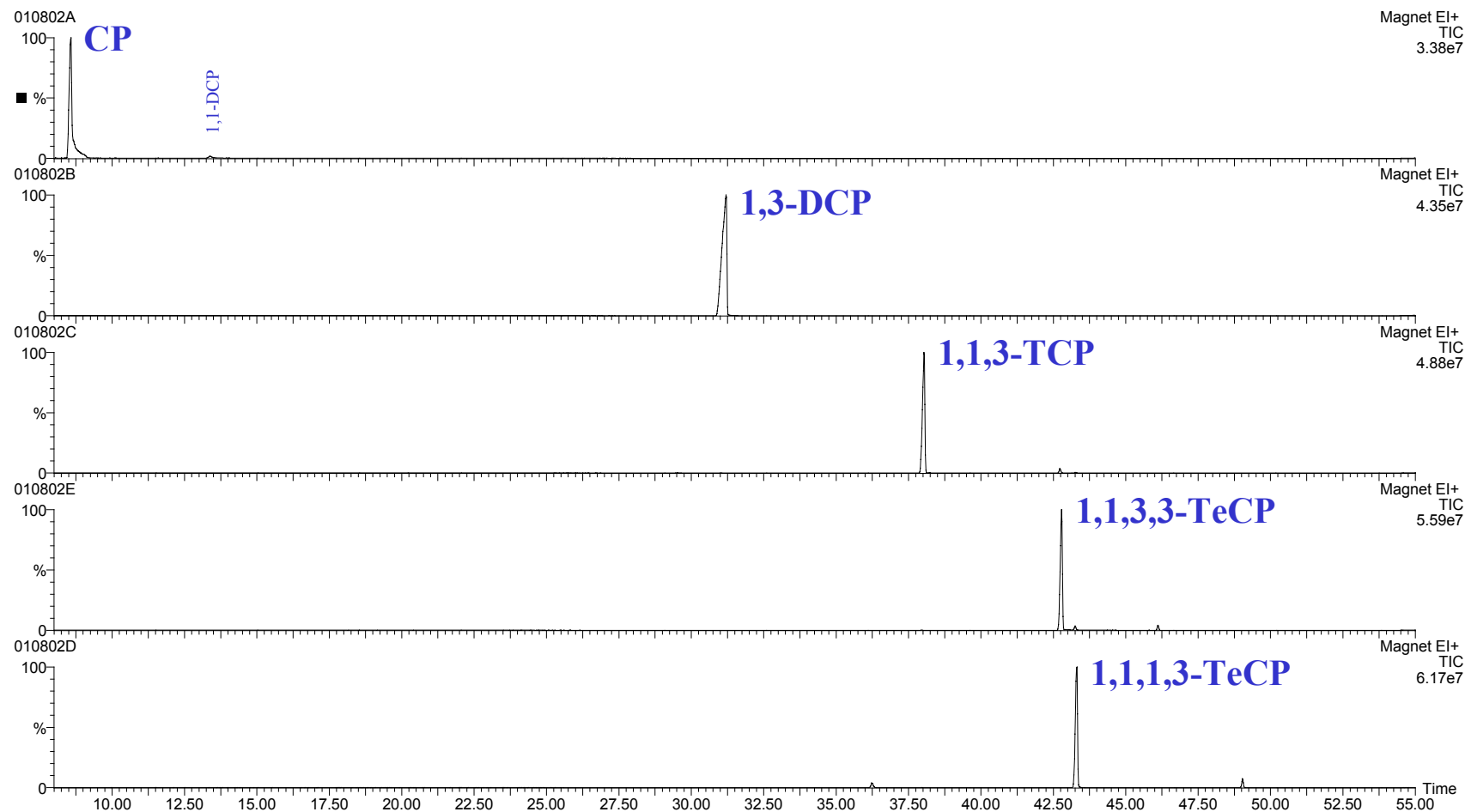


Figure 3. Full-scan total ion chromatograms of chloropropanones from January 2002 stock solution. DBP abbreviations provided in Table 2.

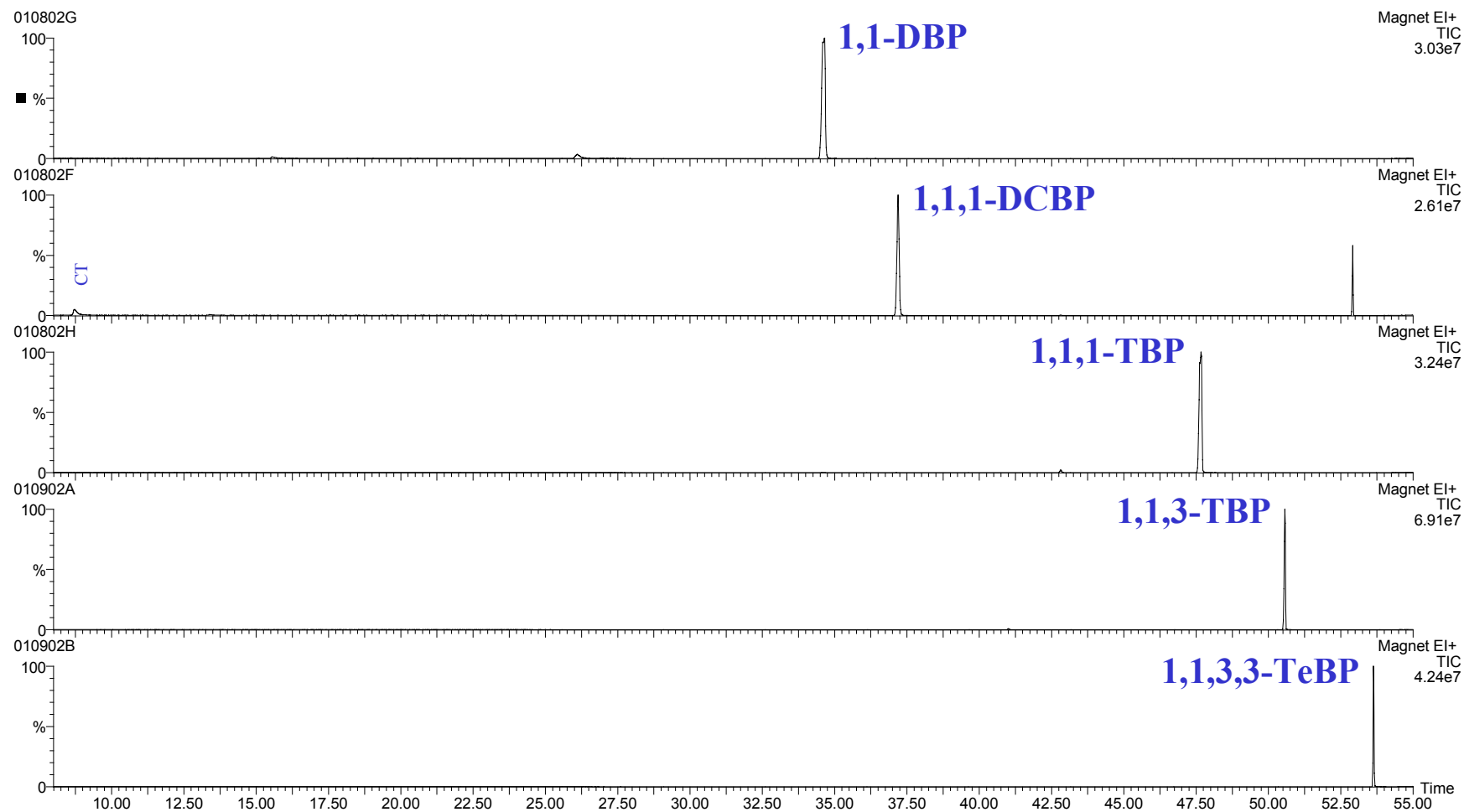


Figure 4. Full-scan total ion chromatograms of bromopropanones from January 2002 stock solution. DBP abbreviations provided in Table 2.

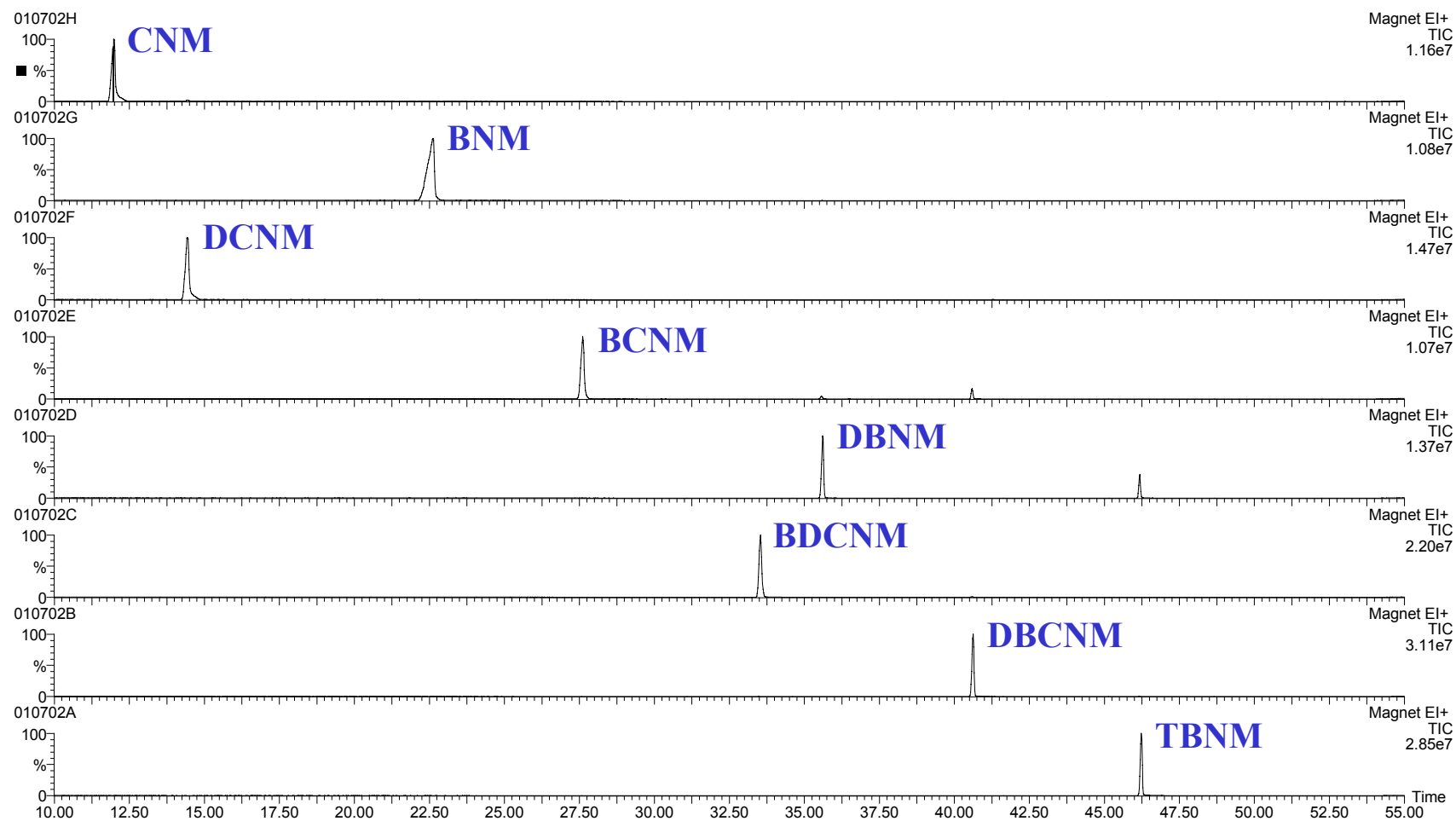


Figure 5. Full-scan total ion chromatograms of halonitromethanes from January 2002 stock solution. DBP abbreviations provided in Table 2.

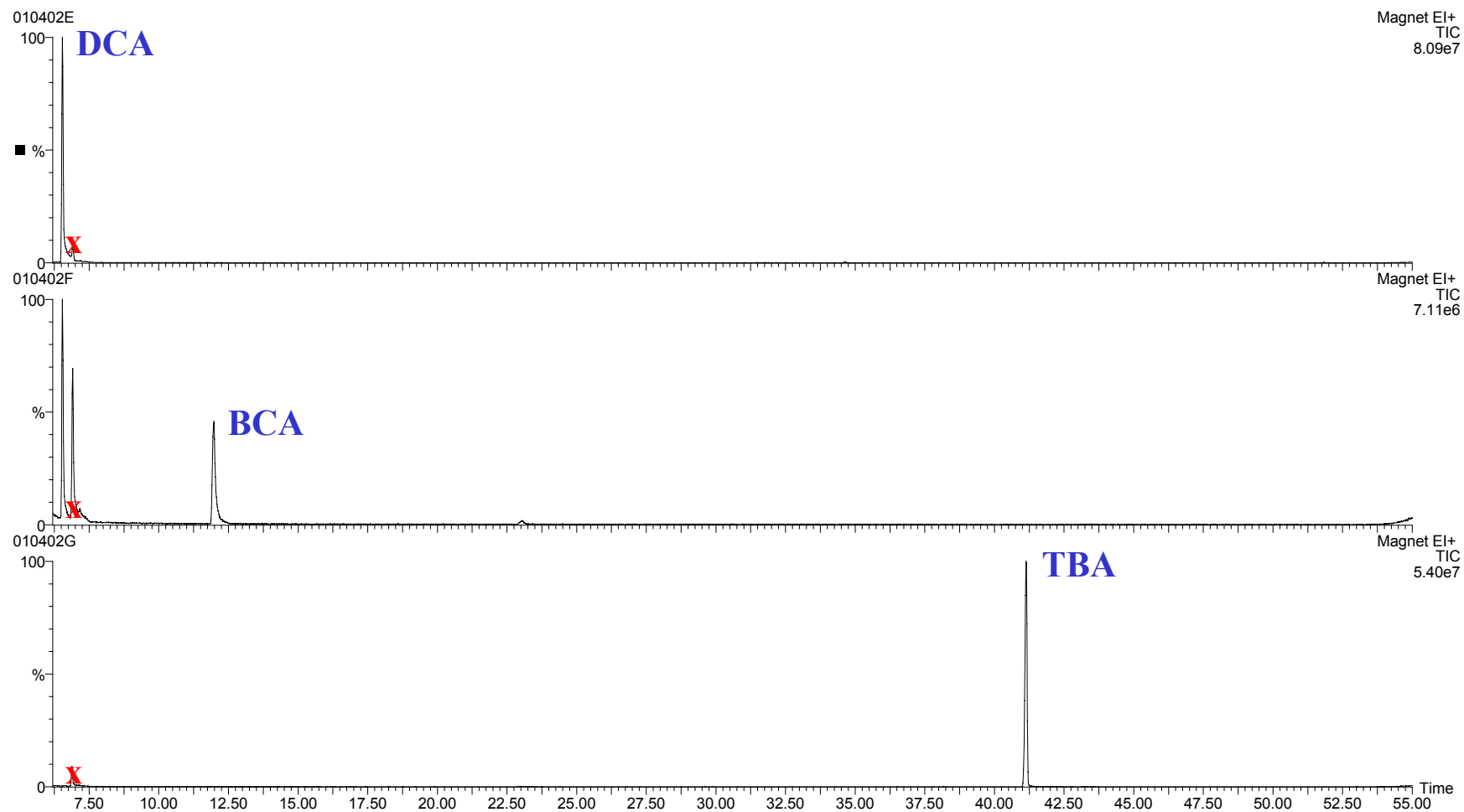


Figure 6. Full-scan total ion chromatograms of haloacetaldehydes from January 2002 stock solution; peaks marked with an “x” are solvent impurities. DBP abbreviations provided in Table 2.

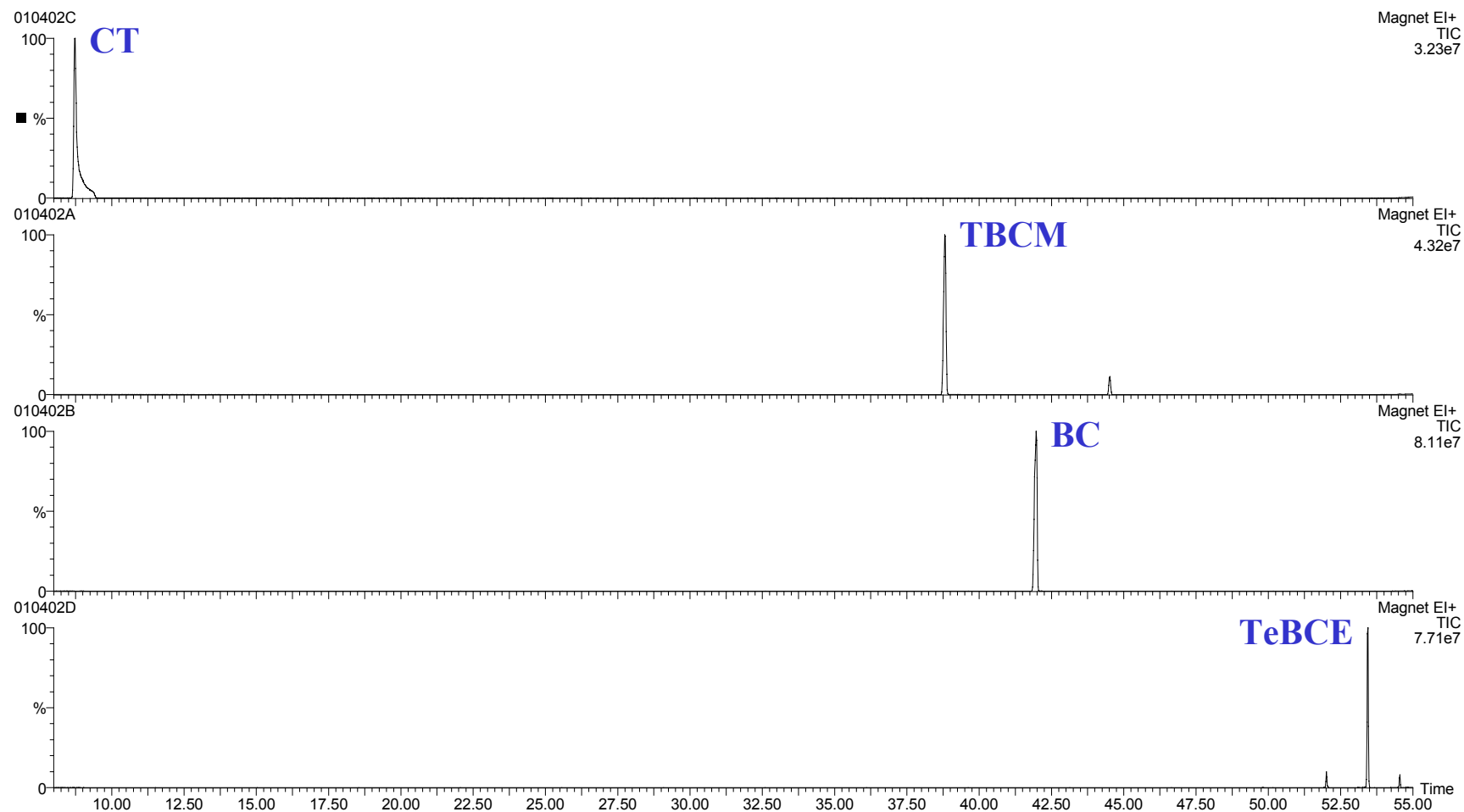


Figure 7. Full-scan total ion chromatograms of miscellaneous compounds from January 2002 stock solution. DBP abbreviations provided in Table 2.

Many of the additional peaks present in the pure compounds resulted from the synthesis procedure, where yields were less than 100 percent. Alternatively, some of the initially pure compounds may have been unstable and degraded over time, forming degradation products, some of which were other DBPs. In addition, some “impurities” were attributed to radical reactions or thermal lability of some compounds in the hot injection port and/or oven of the gas chromatograph (GC) (see section on GC Conditions below).

To obtain the highest accuracy in quantitation, the compound purities were taken into account to determine proper concentration values for standards. Thus, a 1.0 mg sample quantity weighed and diluted to 1.0 mL with solvent produced a 1000 mg/L stock solution. In the case that the compound was 90 % pure, the effective concentration of the stock solution was 900 mg/L.

Tables 2-4 detail DBP purities presented by chemical class. The identification for the impurities for the Winter 2002 quarter stock solutions is presented in Table 2. From the information in Table 2, combined chemical class mixtures were prepared at lower levels, such as 50 mg/L for solid-phase extraction (SPE). These individual master solutions were the spiking solutions used for standards preparation and also for the spiking of samples. The entire 47-compound set for SPE method development was achieved by combining six sets of mixtures that generally contained a particular chemical class. This approach was superior to quantitating individual compounds for every analysis. In addition, compound classes like the halonitromethanes, which had a propensity to degrade faster than other compound classes, could be made up more often as needed. Also, calibration curves could be prepared, which just included specific chemical classes, when more in-depth probing of sample concentrations was necessary.

Correction Factors

There are several ways to correct for concentration anomalies with the standards:

- (1) Calculate the actual concentration of each standard and apply it to the data analysis software.
- (2) Calculate the actual concentration of each standard and generate accurate calibration curves by hand for each compound of interest.
- (3) Determine the adjustment necessary to correct a standard and apply a correction factor to the final results.

The first solution is by far the best because it applies the correction to standards early on in the data analysis process, and all subsequent samples are referenced against the correct curves. This was eventually applied to data generated using the Varian Star Workstation software for results of purge-and-trap (P&T) gas chromatography/mass spectrometry (GC/MS) and SPE-GC/MS. The second solution is extremely time-consuming because all raw areas need to be transported to an alternative software package for graphing purposes. This approach is necessary if the analysis software does not allow customization of individual concentration levels. The third solution is the quickest and easiest to implement because it looks at the overall adjustment for each of the standards and corrects the sample values after the fact.

Table 2. Making of stock solutions in MtBE for Winter 2002 Quarter

Compound	Abbreviation	Stock Date	Weight mg	Conc. (mg/L)	Checked Date	Purity	Adjusted Conc. (mg/L)	Impurities
THM/551B Mix								
Chloroform (trichloromethane)	TCM	-----		5000	-----	99+%	5000	
Bromodichloromethane	BDCM	-----		5000	-----	99+%	5000	
Dibromochloromethane	DBCM	-----		5000	-----	99+%	5000	
Bromoform (tribromomethane)	TBM	-----		5000	-----	99+%	5000	
Dichloroacetonitrile	DCAN	-----		5000	-----	99+%	5000	
Bromochloroacetonitrile	BCAN	-----		5000	-----	99+%	5000	
Dibromoacetonitrile	DBAN	-----		5000	-----	99+%	5000	
Trichloroacetonitrile	TCAN	-----		5000	-----	99+%	5000	
1,1-Dichloropropanone	1,1-DCP	-----		5000	-----	99+%	5000	
1,1,1-Trichloropropanone	1,1,1-TCP	-----		5000	-----	99+%	5000	
Chloropicrin (trichloronitromethane)	TCNM	-----		5000	-----	99+%	5000	
Iodomethane Mix								
Dichloriodomethane	DCIM	12/27/01	6.7	6700	1/3/02	93.3%	6250	
Bromochloriodomethane	BCIM	12/27/01	7.1	7100	1/3/02	96.7%	6850	
Dibromiodomethane	DBIM	12/27/01	8.0	8000	1/3/02	97.2%	7800	BDIM (2.8%)
Chlorodiiodomethane	CDIM	12/27/01	5.3	5300	1/3/02	86.3%	4550	TIM (2.2%)
Bromodiiodomethane	BDIM	12/27/01	7.1	7100	1/3/02	91.5%	6500	DBIM (4.3%), TIM (4.1%)
Iodoform (triiodomethane)	TIM	12/27/01	4.3	4300	1/3/02	99+%	4300	
Haloacetonitrile Mix								
Chloroacetonitrile	CAN	12/27/01	2.8	2800	1/9/02	99+%	2800	
Bromoacetonitrile	BAN	12/27/01	5.3	5300	1/9/02	99+%	5300	
Tribromoacetonitrile	TBAN	12/27/01	6.6	6600	1/9/02	99+%	6600	
Bromodichloroacetonitrile	BDCAN	4/6/01	2.4	2400	1/16/02	91.0%	2200	CT (4.0%), DCAN (2.5%)
Dibromochloroacetonitrile	DBCAN	12/27/01	6.8	6800	1/9/02	41.1%	2800	TBAN (36.3%), DBAN (16.7%), TBM (6.0%)
Haloketone Mix								
Chloropropanone	CP	12/28/01	4.1	4100	1/8/02	98.1%	4000	1,1-DCP (1.9%)
1,3-Dichloropropanone	1,3-DCP	12/28/01	6.2	6200	1/8/02	99+%	6200	
1,1,3-Trichloropropanone	1,1,3-TCP	12/28/01	4.2	4200	1/8/02	97.7%	4100	1,1,3,3-TeCP (2.3%)
1,1,3,3-Tetrachloropropanone	1,1,3,3-TeCP	12/28/01	6.0	6000	1/8/02	94.9%	5700	1,1,1,3-TeCP (2.2%)
1,1,1,3-Tetrachloropropanone	1,1,1,3-TeCP	12/28/01	6.0	6000	1/8/02	91.7%	5500	
1-Bromo-1,1-dichloropropanone	1,1,1-BDCP	12/28/01	4.5	4500	1/8/02	76.2%	3450	CT (7.2%)
1,1-Dibromopropanone	1,1-DBP	12/28/01	5.5	5500	1/8/02	94.1%	5200	
1,1,1-Tribromopropanone	1,1,1-TBP	12/28/01	6.2	6200	1/8/02	98.6%	6100	
1,1,3-Tribromopropanone	1,1,3-TBP	12/28/01	6.6	6600	1/9/02	99.2%	6550	
1,1,3,3-Tetrabromopropanone	1,1,3,3-TeBP	12/28/01	4.0	4000	1/9/02	99+%	4000	
Halonitromethane Mix								
Chloronitromethane	CNM	12/27/01	4.3	4300	1/7/02	98.8%	4250	DCNM (1.2%)
Bromonitromethane	BNM	12/27/01	7.3	7300	1/7/02	99+%	7300	
Dichloronitromethane	DCNM	12/27/01	4.1	4100	1/7/02	99+%	4100	
Bromochloronitromethane	BCNM	12/27/01	5.2	5200	1/7/02	89.5%	4650	DBCNM (8.1%), DBNM (2.4%)
Dibromonitromethane	DBNM	12/27/01	5.9	5900	1/7/02	76.9%	4550	TBNM (23.1%)
Bromodichloronitromethane	BDCNM	12/27/01	5.5	5500	1/7/02	99+%	5500	
Dibromochloronitromethane	DBCNM	12/27/01	6.2	6200	1/7/02	99+%	6200	
Bromopicrin (tribromonitromethane)	TBNM	12/27/01	7.4	7400	1/7/02	99+%	7400	
Haloacetaldehyde Mix + Misc.								
Dichloroacetaldehyde	DCA	12/28/01	5.3	5300	1/4/02	99+%	5300	
Bromochloroacetaldehyde	BCA	12/28/01	1.4	1400	1/4/02	50.1%	700	DCA (47.7%)
Tribromoacetaldehyde	TBA	12/28/01	7.5	7500	1/4/02	99+%	7500	
Tribromochloromethane	TBCM	12/28/01	6.1	6100	1/4/02	92.4%	5650	
Carbon tetrachloride	CT	12/28/01	4.7	4700	1/4/02	99+%	4700	
1,1,2,2-Tetrabromo-2-chloroethane	1,1,2,2-TeB-2-CE	12/28/01	6.0	6000	1/4/02	92.1%	5550	
Benzyl chloride	BC	12/28/01	3.3	3300	1/4/02	99+%	3300	

Table 3. Correction factors for Winter 2002 Quarter when all standards were used

Compound	Purity	Impurities	Contributions for a 10 µg/L Standard	Corrected "10 Std"	Correction Factor
THM/551B Mix					
Chloroform	99+%				
Bromodichloromethane	99+%				
Dibromochloromethane	99+%				
Bromoform	99+%		1.46 ppb from DBCAN	11.46	1.15
Dichloroacetonitrile	99+%		0.27 ppb from BDCAN	10.27	1.03
Bromochloroacetonitrile	99+%				
Dibromoacetonitrile	99+%		4.06 ppb from DBCAN	14.06	1.41
Trichloroacetonitrile	99+%				
1,1-Dichloropropanone	99+%		0.19 ppb from CP	10.19	1.02
1,1,1-Trichloropropanone	99+%				
Chloropicrin	99+%				
Iodomethane Mix					
Dichloriodomethane	93.3%				
Bromochloriodomethane	96.7%				
Dibromiodomethane	97.2%	BDIM (2.8%)	0.47 ppb from BDIM	10.47	1.05
Chlorodiiodomethane	86.3%	TIM (2.2%)			
Bromodiiodomethane	91.5%	DBIM (4.3%), TIM (4.1%)	0.29 ppb from DBIM	10.29	1.03
Iodoform	99+%		0.25 ppb from CDIM; 0.45 ppb from BDIM	10.70	1.07
Haloacetonitrile Mix					
Chloroacetonitrile	99+%				
Bromoacetonitrile	99+%				
Tribromoacetonitrile	99+%		8.83 ppb from DBCAN	18.83	1.88
Bromodichloroacetonitrile	91.0%	CT (4.0%), DCAN (2.5%)			
Dibromochloroacetonitrile	41.1%	TBAN (36.3%), DBAN (16.7%), TBM (6.0%)			
Haloketone Mix					
Chloropropanone	98.1%	1,1-DCP (1.9%)			
1,3-Dichloropropanone	99+%				
1,1,3-Trichloropropanone	97.7%	1,1,3,3-TeCP (2.3%)			
1,1,3,3-Tetrachloropropanone	94.9%	1,1,1,3-TeCP (2.2%)	0.24 ppb from 1,1,3-TCP	10.24	1.02
1,1,1,3-Tetrachloropropanone	91.7%		0.23 ppb from 1,1,3,3-TeCP	10.23	1.02
1-Bromo-1,1-dichloropropanone	76.2%	CT (7.2%)			
1,1-Dibromopropanone	94.1%				
1,1,1-Tribromopropanone	98.6%				
1,1,3-Tribromopropanone	99.2%				
1,1,3,3-Tetrabromopropanone	99+%				
Halonitromethane Mix					
Chloronitromethane	98.8%	DCNM (1.2%)			
Bromonitromethane	99+%				
Dichloronitromethane	99+%		0.12 ppb from CNM	10.12	1.01
Bromochloronitromethane	89.5%	DBCNM (8.1%), DBNM (2.4%)			
Dibromonitromethane	76.9%	TBNM (23.1%)	0.27 ppb from BCNM	10.27	1.03
Bromodichloronitromethane	99+%				
Dibromochloronitromethane	99+%		0.90 ppb from BCNM	10.90	1.09
Bromopicrin	99+%		3.00 ppb from DBNM	13.00	1.30
Haloacetaldehyde Mix + Misc.					
Dichloroacetaldehyde	99+%		9.52 ppb from BCA	19.52	1.95
Bromochloroacetaldehyde	50.1%	DCA (47.7%)			
Tribromoacetaldehyde	99+%				
Tribromochloromethane	92.4%				
Carbon tetrachloride	99+%		0.94 ppb from 1,1,1-BDCP; 0.44 ppb from BDCAN	11.38	1.14
1,1,2,2-TeB-2-CE	92.1%				
Benzyl chloride	99+%				

Adjustments were necessary when all compounds were added together into a single combined solution (Table 3). The column labeled “Corrected 10 Std” represents the concentration of the entire mass of material in a standard that was a sum of all the compounds and impurities. The values for each pure standard were corrected in the process of making intermediate solutions, such as the 50-mg/L compound class mixture discussed above. For example, if the stock solution concentration for chlorodiiodomethane (Table 2) was 5300 mg/L and the compound’s purity was 86.3 %, then the actual, rounded concentration of 4550 mg/L was used to calculate what was required to produce an exact 50 mg/L intermediate standard. Further dilutions were prepared to produce a “10 µg/L” standard. Because of the added impurities, the effective concentrations for some compounds were above 10 µg/L.

When a compound had a 91.0 % purity, 11.0 µg/L of that material was required to achieve a concentration of 10 µg/L for the analyte of interest (e.g., bromodichloroacetonitrile [BDCAN]); whereas, when a compound had a 41.1 % purity, 24.3 µg/L of that material was required to achieve a concentration of 10 µg/L for the analyte of interest (e.g., dibromo-chloroacetonitrile [DBCAN]) (Table 3). In terms of the contribution of impurities, for example, in Winter 2002, 2.5 % of the BDCAN standard was dichloroacetonitrile (DCAN) and 16.7 % of the DBCAN was dibromoacetonitrile (DBAN) (Table 3). Because 11.0 µg/L of the BDCAN and 24.3 µg/L of the DBCAN materials were required to prepare 10 µg/L standards, the contributions of the impurities were in actuality $2.5 \% \times 11.0 \mu\text{g/L} = 0.27 \mu\text{g/L}$ DCAN and $16.7 \% \times 24.3 \mu\text{g/L} = 4.06 \mu\text{g/L}$ DBAN. Even though the purity of the standards for DCAN and DBAN were each 99+ %, the contributions from the impurities in the BDCAN and DBCAN standards, respectively, resulted in the 10 µg/L calibration standard having $10 + 0.27 = 10.27 \mu\text{g/L}$ DCAN and $10 + 4.06 = 14.06 \mu\text{g/L}$ DBAN. Moreover, in some cases, such as for carbon tetrachloride—which was obtained as a high-purity standard—it was also found as an impurity in two of the synthesized standards (BDCAN and 1,1,1-bromodichloropropanone [1,1,1-BDCP]). Thus, the correction factor for carbon tetrachloride reflected the contributions from the two sources of impurity (Table 3).

The correction factors were applied to samples to correct values obtained with the standard calibration curves (Method #3). Alternatively, the factors were applied to the standards to graph accurate calibration curves, and the sample values were read directly from the chart (Method #1).

Finally, only those compounds that were measured with an analytical technique were counted in the correction factor calculations. For example, several DBPs (e.g., DBCAN) were ultimately dropped from the SPE-GC/MS method due to stability issues with the dechlorination agent ascorbic acid. Thus, the impurity contributions of DBCAN—tribromoacetonitrile (TBAN) (36.3 %), DBAN (16.7 %), and bromoform (tribromomethane, TBM) (6.0 %)—were no longer present in the SPE-GC/MS standards. TBAN was also removed from the SPE method, so its correction factor did not make any difference. DBAN’s and TBM’s correction factors of 1.41 and 1.15 were no longer needed with the elimination of DBCAN from the SPE method. Thus, each of the analytical methods required a modification of Table 3 to reflect the compounds that were being included in each method’s combined standard.

GC Conditions

For checking the purity of the standards, the original GC temperature program followed the U.S. Environmental Protection Agency (USEPA) Method 551.1 procedure (Munch and Hautman, 1995), using a DB-1 capillary column (J&W Scientific/Agilent, Folsom, CA; 1.0 μ m film thickness, 0.25 mm ID x 30 m). Initially, the following program was used: hold at 35°C for 22 min; increase to 145°C at 10°C/min and hold at 145°C for 2 min; increase to 225°C at 20°C/min and hold at 225°C for 15 min. The GC injector temperature was 200°C, and the detector temperature was 290°C.

An additional temperature ramp to 260°C was eliminated because all of the compounds eluted during the third step of the temperature program. In addition, an injector temperature of 200°C caused significant degradation of some compounds. The injector temperature was set at 117°C based on an earlier GC method, which prevented the degradation of the thermally labile compound bromopicrin (Krasner et al., 1991). Furthermore, it was possible that some of the “impurities” found were actually radical reaction products formed in a hot injection port. Chen et al. (2002) saw similar behavior to bromopicrin with other trihalocompounds (e.g., the trihaloacetonitriles and other trihalonitromethanes).

The initial purity checks for the study—September 2000 and January 2001—used an injector temperature of approximately 115°C, while work continued to refine the GC temperature conditions. An updated GC program was adopted for the stock solutions starting with the May 2001 set. This new method improved chromatography and helped to eliminate some of the impurities by further dropping the injection temperature—from 115 to 89°C—as well as lowering the oven temperature at which many of the DBPs eluted. The new temperature program was as follows: hold at 35°C for 23 min; increase to 139°C at 4°C/min; increase to 301°C at 27°C/min and hold at 301°C for 5 min. The injector temperature was 89°C.

Table 4 summarizes the purity checks performed during the study. For tribromoacetonitrile, bromodichloroacetonitrile, dibromochloroacetonitrile, and bromopicrin, there was no significant change in purity with the switch from EPA Method 551.1’s GC temperature program to the updated GC program in May 2001. For other compounds, such as the iodomethanes, there was a significant change (improvement) in purity with the updated GC temperature program: up to 25 % for iodoform and 37 % for bromodiiodomethane. Most compounds improved or stayed the same. Only two compounds appeared to diminish in purity after the GC temperature program change: 1,1,3-tribromo-propanone (1,1,3-TBP) and bromochloroacetaldehyde (BCA). Some compounds, such as 1,1,3-TBP, have stability issues, in general. A fresh standard of 1,1,3-TBP from Helix Biotech provided more pure material to complete the last set of Winter 2002 quarter stock solutions. BCA was always problematic because synthesized standards always contained a large contribution from dichloroacetaldehyde (DCA). The small loss in purity for BCA in May 2001 could have resulted from difficulty in quantitation of DCA.

Table 4. Purity checks of synthesized standards

Compound	Source	Purity Sep-00	Purity Jan-01	Purity ^a May-01	Status Summer-01	Purity ^a Jan-02
Iodomethanes						
Dichloriodomethane	Agbar ^b	94.7%				
"	Agbar		New 85.4%	90.2%		93.3%
Bromochloriodomethane	Agbar	75.3%				
"	Agbar		New 89.7%	96.4%		96.7%
Dibromiodomethane	Agbar	13.4%				
"	Agbar		New 86.5%	99+%		97.2%
Chlorodiodomethane	Agbar	65.0%				
"	Agbar		New 52.7%	68.3%		86.3%
Bromodiodomethane	Agbar	Gone				
"	Agbar		New 56.0%	93.8%		91.5%
Iodoform	Mallinckrodt, ^c 99%	74.4%	73.3%	99+%		99+%
Haloacetonitriles						
Chloroacetonitrile	Aldrich, ^d 99%	99+%	99+%	99+%		99+%
Bromoacetonitrile	Aldrich, 97%	99+%	99+%	99+%		99+%
Tribromoacetonitrile	UNC ^e	97.2%	95.2%	99+%		99+%
Bromodichloroacetonitrile	UNC, 93%, < 10 mg	92.6%	92.4%	94.8%	Running low	91.0% ^f
Dibromochloroacetonitrile	UNC, 60%, < 10 mg	41.6%	36.4%	42.1%	Gone	
"	UNC, < 10 mg					New 41.1%
Haloketones						
Chloropropanone	Aldrich, 95%	96.4%	88.9%	98.0%		98.1%
1,3-Dichloropropanone	Aldrich, 95%	99+%	98.4%	99+%		99+%
1,1,3-Trichloropropanone	Fluka, ^g 85%	92.0%	78.1%	99.6%		97.7%
1,1,3,3-Tetrachloropropanone	UNC	90.4%	71.5%	99.0%	Running low	
"	Helix Biotech, ^h 93.5%				New 96.5%	94.9%
1,1,1,3-Tetrachloropropanone	UNC	Not available	66.3%	92.4%	Running low	
"	Helix Biotech, 86.0%				New 82.7%	91.7%
1-Bromo-1,1-dichloropropanone	UNC, 95%	75.0%	63.1%	77.6%		76.2%
1,1-Dibromopropanone	UNC	36.0%	17.0%	38.4%	Running low	
"	Helix Biotech, 92.5%				New 94.0%	94.1%
1,1,1-Tribromopropanone	Can Syn Corp ⁱ	89.0%	48.4%	97.0%	Running low	
"	Helix Biotech, 97.5%				New 98.1%	98.6%
1,1,3-Tribromopropanone	Can Syn Corp	89.0%	84.2%	55.8%	Gone	
"	Helix Biotech, 96.1%				New 97.6%	99.2%
1,1,3,3-Tetrabromopropanone	TCI America, ^j 98%	99+%	99.0%	99+%		99+%

Table 4 (continued)

Compound	Source	Purity Sep-00	Purity Jan-01	Purity ^a May-01	Status Summer-01	Purity ^a Jan-02
Halonitromethanes						
Chloronitromethane	Can Syn Corp	Not available	Not available	99+%	Gone	
"	Helix Biotech, 97.2%				New 98.5%	98.8%
Bromonitromethane	Aldrich, 90%	99.8%	98.7%	99+%		99+%
Dichloronitromethane	Can Syn Corp	99+%	96.5%	99+%		
"	Helix Biotech, 98.6%				New 99+%	99+%
Bromochloronitromethane	Can Syn Corp	Not available	82.8%	97.4%	Running low	
"	Helix Biotech, 87.1%				New 85.3%	89.5%
Dibromonitromethane	Majestic Research ^k	21.3%	77.4%	97.1%		76.9%
Bromodichloronitromethane	Can Syn Corp, < 10 mg	55.8%	Not available			
"	Can Syn Corp, 98.3%			New 99+%		
"	Helix Biotech, 95.8%				New 99+%	99+%
Dibromochloronitromethane	Can Syn Corp, < 10 mg	Not available	Not available			
"	Can Syn Corp, 95.2%			New 99+%		
"	Helix Biotech, 97.1%				New 99+%	99+%
Bromopicrin	Columbia Org Chem Co, ^l 95%	97.9%	95.9%	99+%		99+%
Haloacetaldehydes						
Dichloroacetaldehyde	TCI America, 95%	99+%	92.2%	99+%		99+%
Bromochloroacetaldehyde	UNC, < 10 mg	57.2%	52.0%	45.3%	Gone	
"	UNC, < 10 mg					New 50.1%
Tribromoacetaldehyde	Aldrich, 97%	99+%	91.4%	99+%		99+%
Miscellaneous						
Carbon tetrachloride	Supelco, ^m 99.97%	99+%	99+%	99+%		99+%
Tribromochloromethane	UNC, 90%	73.4%	76.4%	94.9%	Running low	
"	Helix Biotech, 90.3%				New 84.3%	92.4%
1,1,2,2-TeB-2-CE	Can Syn Corp	Not available	Not available	Not available	78.7%	92.1%
Benzyl chloride	Fluka, 99.5%	99+%	99+%	99+%		99+%

^aUpdated GC Program^bAgbar: Aigues of Barcelona (Spain)^cMallinckrodt (Phillipsburg, N.J.)^dAldrich Chemical Company (St. Louis, Mo.)^eUNC: Synthesized by University of North Carolina at Chapel Hill^fStock solution from May 2001^gFluka Chemical Co. (St. Louis, Mo.)^hHelix Biotech (New Westminster, B.C., Canada)ⁱCan Syn: Synthesized by Can Syn Chem Corp (Toronto, Ont., Canada)^jTCI America (Portland, Ore.)^kMajestic Research: Synthesized by George Majetich, University of Georgia (Athens, Ga.)^lColumbia: Synthesized by Columbia Organic Chemical Co., Inc. (Camden, S.C.)^mSupelco (Bellefonte, Pa.)

Problematic Compounds

Hexachloropropanone (HCP) and Pentachloropropanone (PCP). Hexachloropropanone (HCP) may undergo a haloform-type reaction in the presence of nucleophiles; consequently, it can degrade in acetone or methanol. Thus, HCP stock solutions were prepared in MtBE to check retention times. HCP and pentachloropropanone (PCP), however, degraded immediately by 100 % in water under all conditions. Trihalomethyl-ketones may react with hydroxide ions under basic conditions, forming a haloform and a carboxylate anion. Thus, HCP should form trichloroacetic acid (TCAA) and chloroform. This hydrolysis was investigated by spiking distilled water with 30 µg/L of HCP. An aliquot of the 30 µg/L HCP spiked water was acidified, extracted, and methylated with a solution of sulfuric acid/methanol. GC analysis showed the presence of 29.6 µg/L of TCAA, which was also confirmed by GC/MS. A liquid/liquid extraction-GC analysis of another aliquot of the spiked sample showed the presence of 28.6 µg/L of chloroform. Thus, the hydrolysis of HCP, forming TCAA and chloroform, was confirmed. A similar experiment was not performed with PCP-spiked water. However, the expected degradation by-products for this haloketone are dichloroacetic acid and chloroform.

1,1,2,2-Tetrabromo-2-chloroethane (1,1,2,2-TeB-2CE) and 1,1,1,2-Tetrabromo-2-chloroethane (1,1,1,2-TeB-2CE). These compounds presented great difficulty in terms of synthesis. A standard of 1,1,2,2-TeB-2CE was ultimately available in relatively high purity from Can Syn Corp., whereas the 1,1,1,2-TeB-2-CE was available at 28 % purity from Can Syn Corp., and as a small sample from the University of North Carolina (UNC) (Figure 8). The impurities of the first tetrabromochloroethane (TeBCE) sample (Figure 8a) are tribromodichloroethane (TBDCE) and pentabromoethane (PBE), based on the elution order of the compounds and also on the theoretical isotopic patterns for subsequent losses of bromine from each impurity.

A second standard from Can Syn Corp contained both TeBCE isomers together. There is very little difference between $\text{Br}_2\text{CHCBr}_2\text{Cl}$ and $\text{Br}_3\text{CCHBrCl}$. Both have the same mass, which leads to similar retention times, and the two peaks co-eluted, even using the updated GC program (Figure 9b). Furthermore, the mass spectra are nearly the same, with the exception that the $\text{Br}_3\text{CCHBrCl}$ has a small contribution from CBr_3^+ (at only about 8 % of the most abundant peak). Thus, the “3+1” TeBCE (1,1,1,2-tetrabromo-2-chloroethane) cannot be easily distinguished from the “2+2” TeBCE (1,1,2,2-tetrabromo-2-chloroethane).

A decision was made to test for the 1,1,2,2-TeB-2-CE species, in part, because a standard of sufficient purity was available. In addition, it was not clear if the compound in the original study in which it was identified was the “3+1” or the “2+2” species. Any TeBCE compounds that were present would co-elute and be reported as a combined TeBCE result.

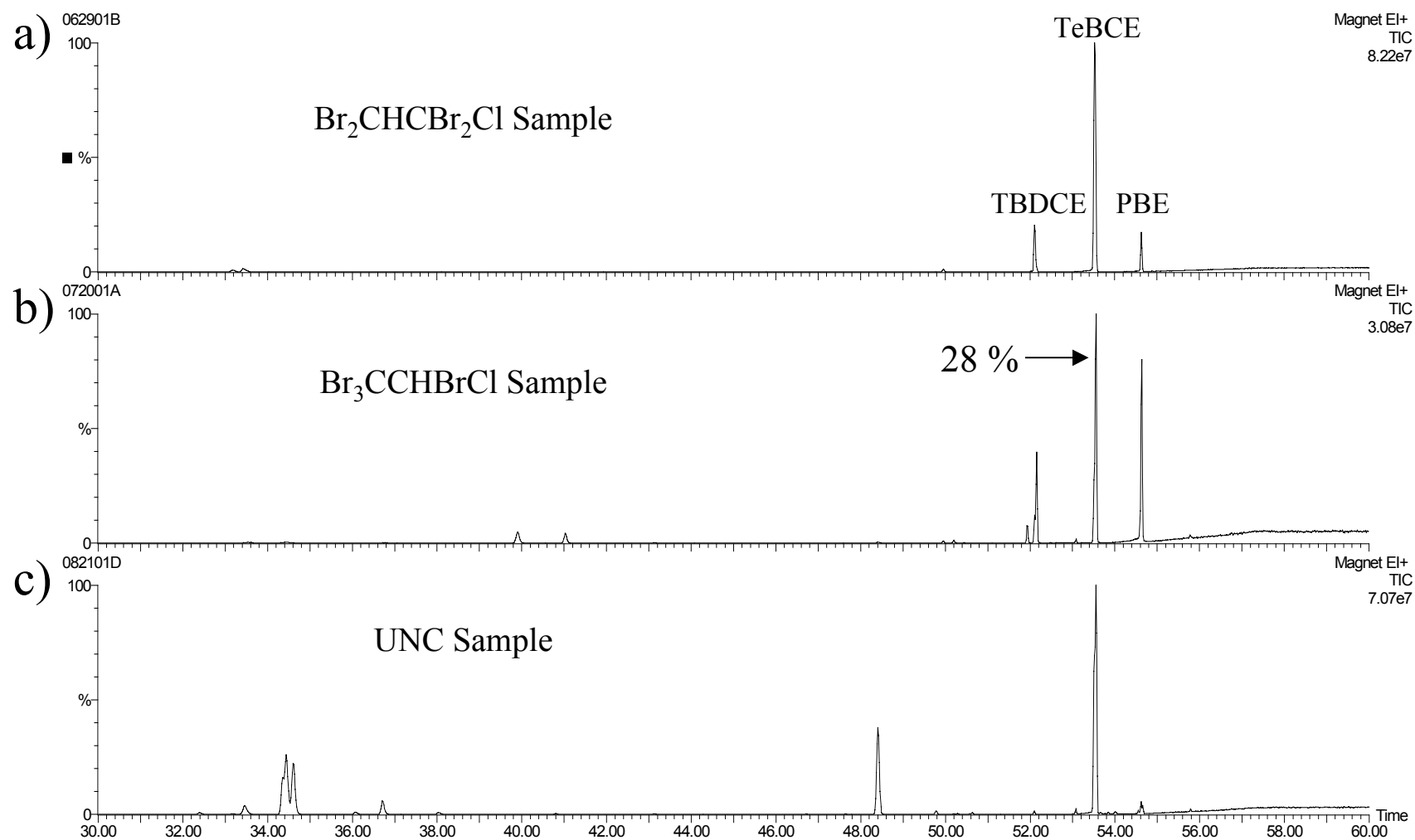


Figure 8. Total ion chromatograms for TeBCE samples: (a) Original shipment of 1,1,2,2-tetrabromo-2-chloroethane; (b) Target compound 1,1,1,2-tetrabromo-2-chloroethane at reported 28 % purity; (c) UNC sample.

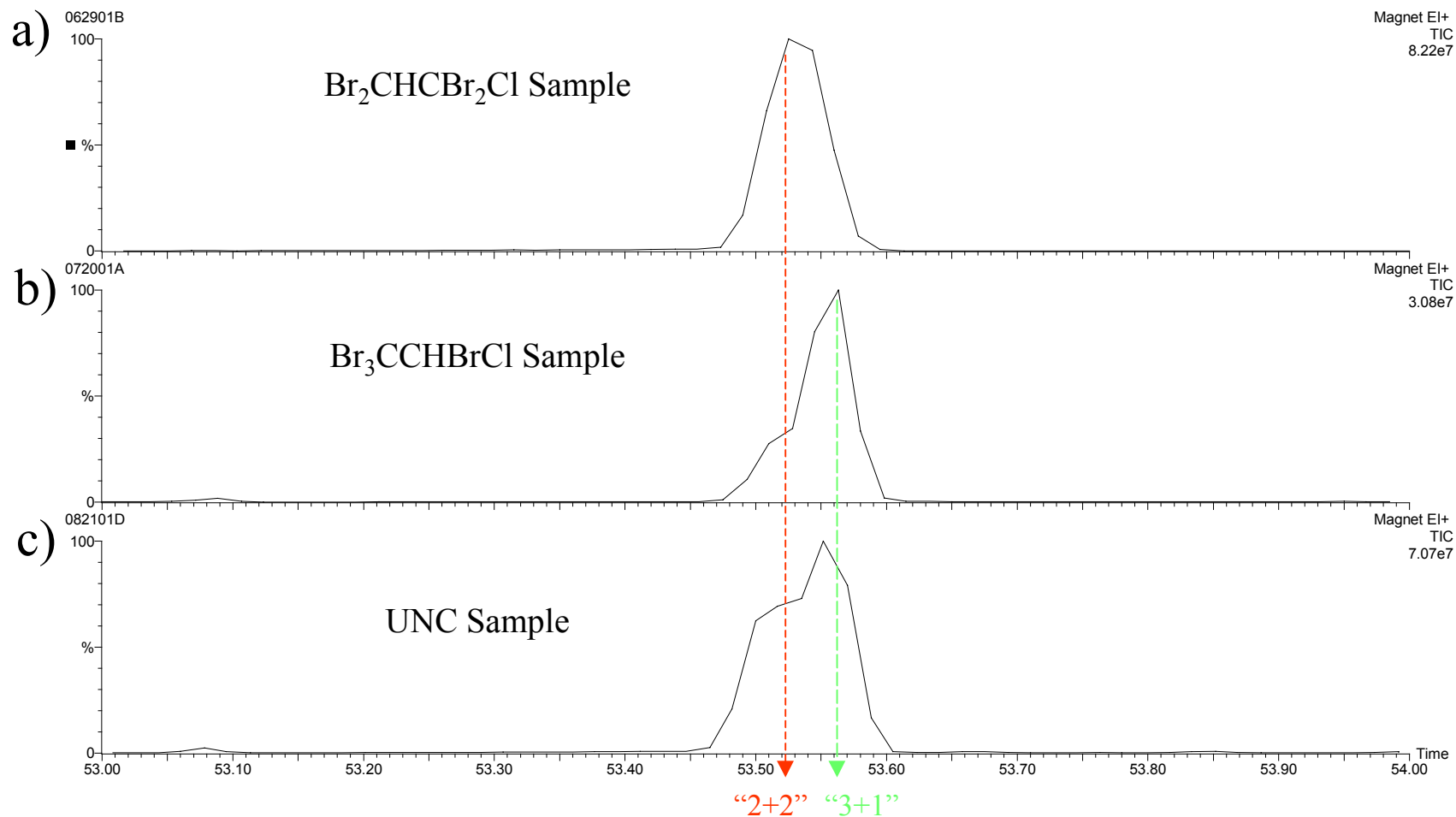


Figure 9. Expanded view of TeBCE samples: (a) Original shipment of 1,1,2,2-tetrabromo-2-chloroethane; (b) Target compound 1,1,1,2-Tetrabromo-2-chloroethane at reported 28 % purity; (c) UNC sample.

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